MICHIGAN ENVIRONMENTAL SCIENCE BOARD

HYDROGEN SULFIDE PANEL MEETING SUMMARY
THURSDAY, JULY 9, 1998
RAMADA INN EXECUTIVE MEEETING ROOM
125 HOLIDAY LANE
HOWELL, MICHIGAN

PANEL MEMBERS PRESENT
Dr. Lawrence J. Fischer, Chair
Dr. David T. Long
Dr. George T. Wolff
Dr. John A. Gracki
Mr. Keith G. Harrison, Executive Director

DEQ/OSEP SUPPORT STAFF PRESENT
Mr. Jesse Harrold, Environmental Officer
Ms. Patricia Hiner, Executive Secretary

I. CALL TO ORDER

Mr. Keith Harrison called the meeting to order at 9:20 am.

II. EXECUTIVE DIRECTOR'S UPDATE

Mr. Harrison discussed the material that had been made available to the Panel in the meeting packets and briefly discussed the literature that had been distributed to date. For the benefit of the public, he emphasized that the Michigan Environmental Science Board (MESB) was a science body and that science and technology, rather than public policy making, would need to be the focus of the Panel's investigation. He also indicated that all MESB Panels operate under the state's Open Meetings Act and public comment would be accepted.

III. MORNING PRESENTATION.

Mr. Ray Vugrinovich (Department of Environmental Quality) provided the Panel with material from the Nebraska Department of Oil and Gas Conservation. In 1983, after a blowup in Alberta involving H_2S, Amoco Canada Petroleum engaged experts to study the effects of H_2S on humans. This lead to three reports, two of which were provided to the Panel: (1) a literature review about the toxicology of H_2S and (2) the results of a field trip by medical personnel to New Zealand where geothermal activity produces continuous H_2S. The Panel was also provided copies of continuous exposure guidelines for H_2S published by the National Research Council in 1985.

Hydrogen sulfide has been reported from Michigan wells since the turn of the century.

Early wells were for salt and water production and were primarily in southeast Michigan and Manistee. Oil and gas wells began operations in the 1930's and by the 1960's, H_2S production in the Detroit River Sour Zone was up to 26 percent by volume of the gas produced. In the 1970's, due to the Niagara Reef trend in northern Michigan, H_2S became well known as a constituent of natural gas especially at processing plants.

Present rules for H_2S, promulgated in1987, were the result of serious odor problems at the Auto Lake Marathon field at the border between Genesee and Lapeer Counties. The rules do not take effect in the absence of odor problems until the H_2S content of the gas being produced reaches 300 parts per million (ppm). This was a compromise between the ten ppm Occupational Safety and Health Administration continuous eight-hour weighted exposure and the lethal concentration of between 500 and 700 ppm.

There is also a radius of exposure which is considered. This is the distance from a point of release at which the concentration of H_2S decreases to a given level. This concept was the result of work done by the National Oceanic and Atmospheric Administration in the 1970's and published in the *Workbook of Atmospheric Dispersion*. The formula for calculation of a radius of exposure involves the concentration and volume of gas that is released in a day. It is an analytic model and makes some extreme assumptions such as flat topography, no temperature inversions, stable atmosphere and little wind. This is the model that had been previously used by the oil and gas regulatory agency in Texas, the Texas Railroad Commission, in its Rule 36.

It was decided in Michigan to classify wells known to contain H_2S into four arbitrary categories based on a 100 ppm radius of exposure. The first category includes those wells that in the event of an uncontrolled release will produce a concentration of 100 ppm at a distance of 300 feet. The second class includes wells that produce this concentration at a distance of between 100 and 300 feet. The distance for a Class III well is between 30 and 100 feet, and for a Class IV well, 30 feet or less. The 300 foot distance for the Class I wells is based on the set-back distances from occupied dwellings, structures used for public occupancy, roads and railroads. It was presumed that by using 100 ppm, anyone who might be exposed to that concentration of gas would have sufficient warning to leave and there would be no long-term health effects.

There were public hearings at seven sites around the state before the rules were promulgated and there was no major opposition expressed. There are currently some modifications to these rules that are being considered. There is a lack of information about long-term exposure to very low concentrations of H_2S. That is why the MESB was requested to look into the subject and determine a range, if possible, of H_2S in air that is safe.

Mr. Tom Godbold (Department of Environmental Quality) discussed some of the proposed changes to the rules for H_2S. One change dealt with H_2S disposal and making sure that any gas is disposed of in a way that limits public exposure. The two primary methods are putting it back down in the ground and burning it. Other methods which might become possible, such as processing equipment, to remove the H_2S would have to be approved by the Department of Environmental Quality's (DEQ) Supervisor of Wells.

Other new rules would address release of hydrocarbons during normal day-to-day operations. These releases have the potential for causing a threat to public health. The newer rules would make odor the standard with no nuisance odors allowed. Mr. Godbold stated that a nuisance odor is difficult to measure. Exact values of H_2S would facilitate development of standards.

IV. PANEL DISCUSSION

Dr. Wolff asked about the distribution of wells into the various categories. He also stated that the four categories were based on something going wrong and asked if there were emissions from the well under normal operations. Mr. Vugrinovich answered that they had approximately 1,300 wells with more than 300 ppm H_2S in the gas produced and thus were under regulation. At this time, they were not broken down into percentage by well class but this could be done. Classification of wells applies to the wellhead itself and there is production equipment specific to each class. Some requirements are automatic shutoff at the wellhead, re-igniters for flares and certain piping to transport the gas. Also there is signage and fencing which are related to work and public safety. Since all wells are equally likely to have odor problems, emission control equipment requirements are virtually identical for all four classes. He stated that there are normally no emissions from the wellhead itself, but many wells have storage tanks which have emissions. Most, if not all, also have flares which cause emissions. Leaks are possible at the wellhead, but these would not be the major source of emissions.

Dr. Wolff asked whether the H_2S was being converted to sulfur dioxide in the flares. Mr. Vugrinovich responded that it was but added that if the flare is extinguished without the gas flow being shut off, there is a H_2S emission.

Dr. Fischer inquired whether there were records of well personnel or nearby residents who had sought medical treatment as a result of exposure. Mr. Vugrinovich replied that there were records of citizen complaints but he was unaware what follow-up had been done. He said that there were records for three industry personnel who had died from H_2S exposure. Two of these deaths had resulted when the worker opened the hatch on a stock tank without wearing the protective breathing apparatus. The third case happened when a worker was attempting to remove a pipe and it broke. He then in a panic removed his breathing device and tried to run away. Mr. Vugrinovich also stated that he suspected there had been dozens or even hundreds of personnel who had been affected and/or overcome by H_2S who had not reported the incidents or sought medical help.

Dr. Wolff asked if air monitoring was required and/or was being done at oil and gas facilities. Mr. Vugrinovich replied that this was not routinely required. In the mid 1980's, a trailer equipped with air monitoring equipment was on location at the Auto Lake field for six weeks in response to citizen complaints. Mr. Harrison requested that representatives from the DEQ Air Quality Division be present to respond to questions regarding air monitoring.

Dr. Fischer asked who was responsible for this monitoring. Mr. Vugrinovich responded that the company will test a well after completion for about 30 days measuring for gas flow rates and H_2S content. The gas flow rate is a daily measurement and the H_2S concentration is measured three to four times during a test. This concentration is not constant and can vary by up to 50 percent over time.

Dr. Long questioned what should be the areas of concern for exposure to low levels of H_2S. Mr. Vugrinovich cited processing plants such as the one at Rose Bush and wellheads which are located close to residential areas. He stated that wherever wells occur there is the potential for a low level exposure. It was then questioned what is meant by low level exposure. Mr. Vugrinovich referred to the California Air Resources Board which established an odor threshold of 0.03 ppm. Dr. Wolff added that a guideline in Michigan for odors was several orders of magnitude less than that, 0.7 parts per billion (ppb).

Dr. Fischer asked whether currently in Michigan 100 ppm was considered a low level safe exposure. Mr. Vugrinovich responded that this was essentially correct; a short time would result in minimal long-term health effects. Exposure to that level of concentration for hours or over weeks and months could result in respiratory disturbances.

V. PUBLIC COMMENT

Ms. Joan Forester read a summary of the composite draft guidelines for sour oil and gas wells and associated facilities in Michigan, March 1976. It included the overall characteristics of H_2S as well as the effects on human health. Ms. Forester also cited an environmental impact statement developed by the Michigan Department of Natural Resources that described the effects of H_2S gas on the surrounding environment. She offered to make these documents available to the Panel. Ms. Forester stated that she was concerned about what she saw as the lack of follow-up after a permit is granted for the development of an oil or gas well. She showed pictures of the results of this development and also spoke of the citizen concern as demonstrated by attendance at public meetings. She appealed to the Panel to take this concern seriously and not get “bogged down in minutia of ppb.” Mr. John Forester added that they had available a health assessment document for H_2S produced by the U.S. Environmental Protection Agency (USEPA) in August 1986. Mr. Harrison responded that the Panel already had been provided that document.

Mr. Bill Myler (Michigan Oil & Gas Association) said that he recognized the need to safely produce H_2S. He stated that this was good business and that it was being done. He said that his industry was regulated by the DEQ’s Geological Survey Division under rules which were updated in 1987 and 1996. He added that the DEQ Supervisor of

Wells has the ability through informative instruction to fill in any gaps in the regulations. Mr. Myler stated the industry goal was to produce H_2S gas without a nuisance odor. He said that 100 ppm is not considered a low level, but rather an emergency-type standard. He said that any industry will have occasional odors but that the current standards were protective of public health. He agreed on the need for an ambient air standard for the occasional incidences where there was a problem. Mr. Myler also offered the assistance of his association and the literature that they had. He referred to the American Petroleum Institute (API) and its ongoing study of the topic. The literature gathered during the three and a half year investigation should be available at the end of this month, with the study complete by the end of the year.

Mr. Keith Schneider (Michigan Land Institute) spoke on the current surge of interest in H_2S which began in August 1996, when a natural gas release from a Niagara well in Manistee Township sent 11 people to the hospital. The gas well was about 300 feet west of a group of homes and businesses. Modeling done by the company responsible and the DEQ set the exposures at under ten ppm. At the time, there were no regulations to deal with a release such as this. Mr. Schneider expressed concern at what he saw as the inaction of the DEQ. He also felt that the DEQ Supervisor of Wells acknowledged the property rights of the mineral owners over public health. He added that citizens and township officials have organized and that public hearings are leading to changes, but these changes need to be more significant.

Mr. Schneider disputed a statement that the health and safety record of the H_2S industry was good. He cited a report, compiled by his group, which he described as the "best chronicle catalog of accidents." In a summary of their findings he stated that 24 people had been seriously injured, at least 260 people had been forced to evacuate their homes, and 35 head of cattle had died from releases of H_2S gas. Mr. Schneider characterized this report as "undisputed" except for ownership of one well which had been erroneously recorded and whether another incident had actually resulted in the release of H_2S. He stated that this showed there was a serious problem in Michigan. He proposed that a threshold should be based on the available data and the regulations set according to that threshold. He also volunteered to facilitate a public meeting in northern Michigan for the Panel to meet with the citizens there. Mr. Harrison requested the actual article from which this summary was taken, and Mr. Schneider agreed to send it.

Dr. Fischer asked if the chronology of accidents and exposures showed whether the situation was getting better or worse or staying the same. Mr. Schneider responded that he felt it was deteriorating. He cited an incident in Addison Township which occurred three weeks previously and resulted in numerous complaints of odors and headaches. He saw one problem as being the reaction time to incidents which he felt was compromised by the reduction in the staff of the DEQ Geological Survey Division. He cited another incident, in Filer Township, where he saw a problem in the sharing of data. In this case, neither the driller nor the DEQ responded to the questions of the citizen involved. Mr. Schneider said that there has since been a directive from the DEQ Director to the Geological Survey Division that such data should be shared.

Dr. Wolff asked for clarification on what happens during an incident and how they are ended. Mr. Schneider answered that each incident is different. He then described the Manistee Township incident where the company was temporarily plugging a deep Niagara well and for 30 minutes there was a planned release of gas. The gas was measured at 900 ppm H_2S. The wind blew the gas east toward homes and businesses. The natural gas company was called to one business and directed the people to leave. People at another business were described as "woozy and headachy." Mr. Schneider said that these people smelled the gas at first, but not later. He stated that the exposure must have been above ten ppm due to evaluation of data which did not show these effects (i.e., people passing out) occurring at ten ppm. Mr. Schneider clarified that although legal at the time, this release of natural gas was made illegal in June, 1997 through a DEQ Supervisor of Well's order.

Mr. Schneider stated that other instances of excursions were due to plant malfunctions. A current concern is the expanding transport system of pipelines. While there is a low actual risk, there is a high potential risk. Of particular concern is the reserves which contain very high levels of H_2S. He cited a well in Filer township, drilled in the early 1990's, that has 40,000 ppm H_2S and is in a residential area. This is a potential problem, especially when considering the accident at Manistee. He suggested a prevention program with a threshold of public health exposure to deal with this problem.

Mr. Myler commented on the previous question as to whether problems are increasing in magnitude. He stated that in Manistee County drilling has decreased from 150 Niagaran wells in 1985 to 12 in 1997 and production of natural gas decreased from 45 to 15 billion cubic feet. He stated that this demonstrated a decrease in the size of the problem. The incident in 1996 was significant and highlighted a gray area, but that the DEQ Supervisor of Wells closed this gap in the regulations. He characterized accidents as "infrequent" emergency situations and not related to daily operations or ambient air standards. He added that one recent incident involving chemicals at a hardware store forced the evacuation of 300 to 400 people; more than all those evacuated due to oil wells in Manistee County.

Mr. Tim Baker (West Bay Exploration) disputed the record compiled by Mr. Schneider. He stated that misinformation supplied by Mr. Schneider had caused damage to his company. He asked the Panel to investigate rather than accept the data which had been presented. Mr. Baker also said that he felt the oil and gas industry had been unfairly targeted. He referred to the safeguards put in place by the DEQ regarding emissions and offered to provide tours of his facilities. He stated that these facilities had odor sensors and tank monitoring systems. In response to what records there were from these sensors Mr. Baker said that there were records of calls to the office. He added that odors are not always H_2S and many of these complaints could be due to general hydrocarbon odors.

Mr. Baker clarified that in response to a complaint, there will be a sample taken of the gas. However, there is not an air quality monitor that continually samples the air and creates a record. The odor sensors are actually chromatographs that sense any combustible gas capable of producing an odor and will shut the facility down upon detection of a hydrocarbon odor. He added that most of the sources for odors are from facilities, rather than wellheads and so that is where most of the sensors are placed. He stated that the sensitivity depended on things such as air currents.

Dr. Long indicated that most of the public comment thus far was in regard to high level exposure. Mr. Harrison requested that public comments stick with what the Governor charged the MESB to investigate; health impacts of long-term low level exposures.

Dr. Fischer requested H_2S monitoring records. Mr. Baker said that he would send what monitoring information they had for their wells.

Dr. Wolff requested clarification on the determination of the placement of monitors at a facility. Mr. Baker explained that upon completion of a well, ground water monitoring wells are planned to establish ground water gradients and generally monitor water quality. After the DEQ looks at this plan for the facility, odor detection devices are placed in areas determined to be sensitive or in wells which might likely have a problem. They would typically be placed around the tanks, separation equipment and the flare stack. The flare stack is where waste hydrocarbons can be burned by mixing one part hydrocarbon with nine parts air. Ultraviolet sensors and heat sensors here shut the entire well down if the flare goes out.

Mr. Don Mazuchowski (Michigan Public Service Commission) commented on the sensors. He stated that at the wells that they had been working with this year, the producers have installed three sensors around each wellhead and more at the facility where they take the gas and at the storage tanks. The sensor will detect down to at least one ppm, the pumper will be called out at three ppm and at ten ppm it shuts the facility in. These are small electronic sensors that detect H_2S and are placed at mainline valves and all above-ground structures. Due to the added expense, most of these do not have recorders attached.

Mr. Mazuchowski said that public calls in response to incidents are recorded and are thus an indication of the problems. He added however, that at one ppm the sensors are triggered faster than people could smell the gas because smelling is around ten. Dr. Gracki countered that smell is 0.03 ppm to which Mr. Mazuchowski responded that the gas is usually diluted by the time it leaves the site whereas the monitor is placed right at the source. He added that he did not have any knowledge that recordings had been made and kept from these sensors, but he would check further.

Dr. Wolff questioned whether the sensors were new and/or recently made a requirement. Mr. Mazuchowski responded that he felt they had been around for a long time and that they were required, not by law but by their recommendations. He added that he only dealt with well operations and that the DEQ was responsible for the drilling of the well. Mr. Vugrinovich clarified that there was no ambient air monitoring that was required by law of wells producing H_2S, although this could be specified in an agreement between DEQ field staff and the owner of the well. He added that the Public Service Commission has control over wells that produce dry natural gas while the DEQ Geological Survey Division has jurisdiction over oil wells.

Dr. Long asked what the sensors would shut down. Mr. Mazuchowski responded that the whole facility and the production of gas from that well would be shut down. A sensor on the gas pipeline would only shut down the pipeline, but the pressure build up would eventually shut the well off. A rupture in the pipeline where there are no sensors would not cause the pipeline to be shut down. Mr. Mazuchowski offered to provide a technical description of the sensors including the temperature specifications, adding that they work at temperatures well below freezing. Mr. Baker added that there were mechanical backups to the sensors and multiple pieces of equipment for safety including extra lines to protect against digging accidents.

Mr. Brian Jennings (Premark Corporation) stated that he was involved in the concrete pipe and concrete manhole aspect of the St. Claire sewer industry. He said that he could provide information on the process of H_2S generation in the sewer system.

Mr. Jim Hull (Concrete Pipe Association of Michigan) questioned the accessibility of the meeting minutes. Mr. Harrison informed him that meeting summaries would be available and that having his name added to the MESB mailing list would facilitate this.

VI. PANEL DISCUSSION OF CHARGE

Dr. Fischer stated that the charge from the Governor was fairly narrow, the health effects of low level ambient air exposures of H_2S. He questioned whether the scope of the Panel's investigation should or could be expanded as the information presented today reflected the public concern over higher, accidental exposures. Mr. Harrison reminded the Panel that the acute effects of exposure to high levels of H_2S were well documented and that is why the Panel was specifically being asked to look at long-term effects of exposure to low levels.

Dr. Long suggested that the exposure levels should be looked at as a continuum, however. He cited the Nebraska report where they started at ten ppm over a minute and went down to 0.005 ppm over 30 days. He questioned whether it was possible for someone to be exposed without being aware of it since the smell threshold is so small. Large turkey and/or dairy farms were given as an example by Dr. Gracki, where workers could become used to the odor and thus be chronically exposed to and absorb a level of H_2S gas which is below the level considered dangerous. Dr. Gracki also concurred with considering a continuum of exposure levels and said that setting a low long-term threshold would impact the higher levels, perhaps lowering them.

Dr. Wolff added that there is a natural background of H_2S of probably a ppb or less. He pointed out that the lower numbers picked by Nebraska were based on corrosion of metals and the Panel's charge was health.

Mr. Harrison asked if there was a need to contact experts in agriculture and waste disposal to get data on how the numbers for background H_2S are generated. Dr. Wolff responded that he had that information and could make it available, but he requested that the DEQ Air Quality Division meteorologists provide data on the expected emissions from various types of leaks.

Dr. Long asked for clarification on the classification of wells into four categories. He questioned whether the amount of H_2S produced impacted the distance from the population at which the well could be placed. Mr. Vugrinovich indicated that the setback distance was a fixed number, 300 feet for the wellhead itself, and the well classification had no bearing on this. There could be certain equipment required as well as signs, fencing. This could possibly change depending on the level of concentrations which the Panel decided were safe for someone to breathe. However, turning these recommendations into regulations is an enormous leap. It was reiterated that ten ppm was not lethal, but there were still offenses at that concentration.

Dr. Wolff added that there was a range of sensitivity for various individuals. He questioned the concentration of H_2S at 300 feet for the four different categories of wells, since being able to predict this is crucial to estimating the exposure to the general public. Mr. Vugrinovich answered that it depended on the concentration of H_2S in the produced gas and the volume released at the point of emission. It would be necessary to set up a monitoring system at 300 feet, or use numerical modeling. Dr. Fischer suggested placing a sensor at 300 feet downwind of the well and setting it to trigger a shutdown of the well at levels consistent with projected health effects. Dr. Gracki added that it should be specified in the regulations where the sensors were to be put.

Mr. Mazuchowski commented that the normal operation of the well do not emit any H_2S, and that the USEPA has guidelines for emergency releases. However, he also stated that filling a truck with liquids from the well is part of the normal operation and does produce emissions which are sent to a flare to burn. There could also be a tiny amount of H_2S leaking through fittings, but under normal operating conditions it is not enough to smell. Once burned through the flare, the emission is sulfur dioxide, which also smells bad, rather than H_2S.

Dr. Fischer mentioned places in Michigan that have an odor connected with gas production, some of which is probably H_2S. Mr. Mazuchowski said that most of the odor is from sulfur dioxide and mercaptans. Dr. Fischer questioned the availability of sensors to detect the amount of H_2S in places that have a constant nuisance odor. Mr. Mazuchowski said that this might be possible. However the odors which can be smelled; i.e., at 0.03 ppm, are below detectable levels by the meter (below one ppm). Dr. Wolff agreed that mercaptans and other reduced sulfur gases of concern emitted from the same sources complicate the issue.

Dr. Fischer asked whether emissions of H_2S from the wells contribute to the ambient air concentrations. It was felt that there were not data available to answer this.

Mr. Harrison questioned whether the impacts of high and low level exposures occurred via the same mechanism. Dr. Fischer responded that the long term effects of high exposure to H_2S were not from the H_2S itself, but from the lack of oxygen, the hypoxia that the H_2S acute exposure produces. This makes it difficult to extrapolate the effects of low levels based on high level exposure long-term effect.

VII. AFTERNOON PRESENTATION

Dr. Adi Pour (Nebraska Department of Health and Human Services) indicated that her presentation would be on the human health effects that result from ambient air exposure to H_2S at low concentration over extended periods of time. Her interest in this began in 1994 in Nebraska due to great public concern. A group of citizens felt that they had adverse health effects from the H_2S produced in the tannery lagoons near their homes. There are no national ambient air exposure standards for H_2S. This prompted a review of the available scientific literature.

Hydrogen sulfide is a colorless, odiferous, irritating and flammable gas. Inhalation is the major route of absorption. Oral absorption is not well documented although it is possible for people who are exposed to liquid manure. Dermal absorption is unlikely. One study on guinea pigs demonstrated minimal dermal absorption. Upon inhalation, H_2S is widely distributed in the human body. Post-mortem examination of people exposed to fatal concentrations has revealed H_2S present in blood, liver, kidney, brain, lung, heart and spleen. Excretion of H_2S is mainly in the urine. Fifty percent is excreted in the urine in 24 hours, with a minor component being pulmonary excretion.

There are three pathways of H_2S metabolism: oxidation, methylation and reaction with metalloproteins. Oxidation is the major pathway of H_2S metabolism and involves the mitochondria of the liver. Inhaled H_2S is transformed in the liver into a thiosulfate which is further oxidized to a sulfate which is excreted by the kidney in the urine. A minor pathway is methylation which is thought to be how endogenous H_2S, produced by the gut, is metabolized.

There are metabolic pathways which can be considered toxic. Hydrogen sulfide can combine with some of the metalloproteins. The main toxic pathway for these disulfide containing proteins is the interruption or inhibition of the cytochrome oxidase enzyme. This results in less oxygen being transferred through the electron transfer system which can result in anoxia. Hydrogen sulfide toxicity at high concentrations is also seen in the increased respiration which results from stimulation of the carotid bodies.

Acute exposure is defined as a single exposure to a high concentration producing rapid signs. For H_2S there is imminent death occurring at approximately 5,000 ppm. This is sometimes called a knock down because it occurs instantaneously. There is respiratory paralysis at about 1,000 ppm and breathing can stop after prolonged exposure at 500 ppm. These levels are not precise, however. All of these acute effects are due to respiratory paralysis.

Subacute exposure can be considered as continuous exposure to mid-level or repeated exposure at higher concentrations. This can include levels of 250 down to ten ppm. Primary health effects of these exposures are to the eyes and include tearing, conjunctivitis and inflammation. Certain exposures produce a “gas eye.” After the eye, the system most sensitive to irritant effects is the respiratory system. Subacute exposure can result in rhinitis, laryngitis and pharyngitis. The most serious health effect at these levels is pulmonary edema after prolonged exposure. This can actually be a lethal effect from exposure at 250 ppm.

Scientific information can be gained from animal studies. The Agency for Toxic Substance in Disease Registry (ATSDR) based its 365 day standard on the Curtis (1975) study. In this study, pigs were exposed to 0.9 ppm H_2S for 17 days without any effect. The ATSDR then used a safety factor of ten and came up with 0.09 ppm as the 365 day minimal risk level (MRL).

Another study, by Torrans (1982), looked at catfish and determined that inhibition of cytochrome oxidase resulting in increased lactate was occurring in this species as well. This study found a dose response between H_2S and the anaerobic end product.

Hannah and Roth (1991) did a study in which they exposed pregnant rats to different concentrations of H_2S over long periods of time. Unfortunately, the mothers were not examined. However, alterations were found in the pups. There were statistically significant differences in the length of the purkinje fibers as compared to control levels. This could be relevant in considering whether developing children are at a higher risk for exposure.

The health effects of H_2S include many nonspecific symptoms such as fatigue, headache, sore throat, nausea, insomnia, confusion, eye irritation and gastrointestinal disturbance. Much information about these effects has come from occupational studies of the pulp industry in Finland. Questionnaires were sent to pulp industry workers and the results were compared to a group working in a different type of industry. One limitation of the occupational studies is that they are usually considering a healthy work force which has chosen to work there.

There are also epidemiological studies that look at the general population. Homeowners might not be able to easily leave the area of exposure. A 1964 study was done in Terre Haute, Indiana on an industrial waste disposal lagoon. Although exposure concentrations were not precise, and comprised a large range, the symptoms experienced by the citizens in the area were similar to those seen in the industrial studies. These symptoms included nausea, vomiting, diarrhea, abdominal cramps, shortness of breath and other respiratory problems.

Epidemiological studies have also been conducted in South Karelia, Finland, near the pulp mills. Low levels with an annual average of five ppb resulted in general symptoms such as eye and nasal irritation, respiratory symptoms and headache. However, there were other chemicals, mercaptans and carbonated sulfides, in the air and it was not possible to measure only the H_2S. Also, at five ppb there is an odor and this could cause people to assume effects. While epidemiological studies can provide supporting evidence, they have several drawbacks. The genetic makeup of different populations can vary and there may be underlying effects that are not measured. Additionally, epidemiological studies often do not have dose response curves which are important for the development of standards or regulations.

Good information can be obtained from controlled clinical studies. Research has been conducted by Bhambani (1991, 1994 and 1996), an exercise physiologist from Canada. Beginning in 1991, Bhambani had volunteers exercise on a bicycle and he would measure their pulmonary function after exposure to H_2S. This was inhaled through the mouth in order to avoid the smell. Five tests were conducted on each individual with exposures of zero through five ppm over a period of 25 minutes. What he found was that there was no change in heart rate or pulmonary function, although there was a significant increase in blood lactate at five ppm. Lactate is the end product of anaerobic metabolism, the pathway used when inhibition of the cytochrome oxidase system results in a lack of oxygen for aerobic metabolism.

In a second study, Bhambani (1994) had the subjects exercise at half of maximum output while exposed to ten ppm, the occupational standard. He concluded that there were no adverse health effects since there were no changes in oxygen uptake, carbon dioxide production, respiratory rate, heart rate or blood pressure. In 1996, Bhambani used a 15 minute test. This also showed no pulmonary changes. Also in 1996, Bhambani measured the change in some enzymes in muscle biopsies at five ppm over 30 minutes at 50 percent maximum output. He found decreases in cytrate synthase and cytochrome oxidase. He also found an increase in lactate and lactate dehydrogenase.

A 1990 study by Jappinen measured respiratory functions of pulp mill workers at the end of work and after one day off and compared them to asthmatics who were exposed in the laboratory to two ppm for 30 minutes. There were no respiratory function or bronchial response change noted in the pulp workers. However, two of the ten asthmatics had 30 percent bronchial restriction suggesting an added sensitivity of asthmatics and others with underlying chronic disease.

Regulatory challenges include whether to regulate based on nuisance, such as odor, or based only on health effects. The odor threshold for H_2S is very low. There is also olfactory paralysis at high concentrations resulting in an inability to detect the odor. Also, the odor changes at higher concentrations, becoming sweet rather than the familiar rotten egg odor. And there are different perceptions of the same odor. In New Zealand, geothermal wells with the same odor are not considered offensive since these wells produce baths which are considered healthful.

Also to be considered are the economic effects of regulation as well as the psychological effects. There are also aesthetic effects to consider, and whether there is actually sufficient science to make an informed decision. In addition, is it a single compound or a mixture which needs to be regulated? The ambient air quality standard developed in Nebraska was for total reduced sulfur compounds because H_2S was too difficult to measure separately. In Nebraska, it is the Environmental Council which approves any environmental regulation. It approved a two-tiered standard. There is an acute standard of ten ppm at one minute. This is based on the National Institute for Occupational Safety and Health recommendation of 100 ppm for a healthy worker with a safety factor of ten added to make it safe for the general population. Environmentalists felt that it was not safe enough and so cut it in half resulting in a standard of five ppm. The 30 minute standard was developed from the Bhambani studies which showed a no observed adverse effect level at two ppm. Since these were healthy volunteers, a safety factor of ten for sensitive individuals was added. Another safety factor of two was added, resulting in a one ppm 30 minute standard. While other states have a wide range of standards, Nebraska decided on a short-term standard rather than one averaged over a year. This would be the most protective of public health considering the spikes in H_2S levels which are seen there.

VIII. PANEL DISCUSSION

Dr. Long questioned which point sources had been monitored. Dr. Pour answered that while sewage treatment and pesticide plants are also sources, some of the biggest point sources are open lagoons from tanneries. This industry realizes that there is a problem, however, it would take millions of dollars to cover the lagoons.

Dr. Pour stated that in formulating their standards, some industries had been exempted. Agriculture was exempted to a certain degree and some oil wells were also exempt. Additionally, municipalities were given time to come into compliance. She added that some of the oil wells in her state were in uninhabited areas and produced no public exposure to H_2S. However, Dr. Pour stated that she felt any high level exposure to H_2S should be regulated, regardless of the source.

Dr. Wolff questioned whether there were data available on concentrations near these sources. Dr. Pour responded that these measurements were taken by the Nebraska Department of Environmental Quality and the request would need to be made to them, but that this was public information. She added that there was no monitoring around any gas wells, although they were starting to monitor around sewage treatment plants. Dr. Pour stated that she had no knowledge of any states which might have monitoring programs. She said that the difficulty was in measuring the H_2S.

When questioned about what started the interest in H_2S, Dr. Pour attributed it to concerned citizens who felt that they had symptoms from exposure. The exposure was due to lagoons located close to residential areas. As a follow-up, the ATSDR might do a health study with this group. This would include neurological tests with the results compared to a similar but not exposed group. A study such as this would add to the scientific literature which currently does not have a lot of good information on chronic low level health effects. There is however, one individual in southern California, Kate Kilburn, who has examined quite a few neurobehavioral tests on this type of people in conjunction with a lawsuit there.

Dr. Long asked whether the egg industry had been exempted from regulation. Dr. Pour answered that the commercial animal feeding operations were not exempt, but that smaller, family-run operations would be. She said that she did not have data on occupational exposure in the egg industry. She stated that Iowa had done studies on this.

Dr. Fischer questioned why the elderly had been included in the sensitive subpopulation. Dr. Pour responded that it was felt that the elderly may have depressed oxygen capacity in some of their tissues and thus could be more sensitive to oxygen deprivation by H_2S. She added that while in general the elderly and children are considered to be more sensitive to exposure, this is not always based on science.

Ms. Renee Scarporn asked whether infants were not getting a more toxic level, a higher concentration of H_2S due to their smaller body weight and faster respiration. She compared it to giving an infant an adult dose of medication. Dr. Pour answered that some of the effects of faster respiration were accounted for in the Bhambani study by having the subjects exercising. Also, the consideration for the smaller body weight of a child was taken into consideration in adding a factor of ten for a safety factor. These dosages are not comparable to medications since H_2S is inhaled, whereas medications are ingested and taken into the body through a variety of mechanisms. Dr. Fischer added that there is no simple adult/child conversion factor for medications. All children's doses of medication are now developed by clinical trials.

Dr. Fischer stated that the effect demonstrated by the data from Bhambani was the inhibition of cytochrome oxidase and the formation of lactate. He asked whether this was outside the range that might occur under normal conditions, adding that exercise will normally produce some level of anoxia. Dr. Pour agreed that exercise produced lactate and this could be evidenced by muscle cramps. She said that what was important was that there was no increased lactate present at two ppm or lower. It was only seen at the highest concentration of five ppm. The tests were also on different days, eliminating the possibility of an effect from accumulation.

Dr. Fischer asked whether the effect seen was a toxic effect. Dr. Pour answered that in setting regulations, it is necessary to look for the first sensitive effects that are visible and that standards can be established at the lowest observed adverse effect level. This adverse effect can be something such as weight loss in experimental animals. Inhibition of cytochrome oxidase is the first measurable physiological effect of H_2S. Dr. Pour stated that this is an adverse effect based on the effect of respiratory paralysis at acute levels due to oxygen deprivation. However, the change that occurs at low concentrations is not an irreversible effect; it is not permanent.

Dr. Fischer questioned whether there was any evidence of a non-reversible effect resulting in permanent damage at low concentrations. Dr. Pour said that she had not been able to find any evidence of this. She had found one study which showed effects to the nasal epithelial cells of rats. However, the relationship of rats which are nose breathers with humans is questionable. Dr. Pour stated that the only non-reversible effects were caused when the brain had been deprived of oxygen and resulted from acute exposure at very high concentrations. Dr. Fischer added that the studies on pregnant rats showing detrimental effects to the offspring demonstrated a permanent effect, however, maternal hypoxia cannot be ruled out as the mothers were not examined.

IX. PANEL ASSIGNMENTS

Responsibility for the various parts of the report were assigned as follows:

Dr. Wolff agreed to provide an overview of the sources of H_2S. It was suggested by Dr. Fischer that due to the large hog operations, Iowa might have done some monitoring of agriculture lagoons for H_2S. Dr. Wolff also agreed to provide a short description of the atmospheric chemistry of H_2S.

Dr. Gracki indicated that he would report on the measuring of H_2S along with the sensitivity limits.

Dr. Long was asked to provide information on exposure incidents and monitoring of H_2S exposure in Michigan.

Dr. Fischer volunteered to write on the fate of H_2S in the body as well as H_2S toxicity, acute and chronic.

Mr. Harrison would provide the introductory material and serve to bring the entire report together.

X. NEXT MEETING DATE

Mr. Harrison indicated that his office would contact the Panel regarding the next meeting. Dr. Wolff requested input from the DEQ Air Quality Division for the next meeting . One question for them would be the rationale for the standards which had been chosen in Michigan. Dr. Gracki said that he would check on the availability of an expert on the analytical detection of H_2S and the sensitivity of the sensors.

XI. ADJOURNMENT

The meeting was adjourned at 3:00 PM.

Respectfully submitted,
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Executive Director
Michigan Environmental Science Board